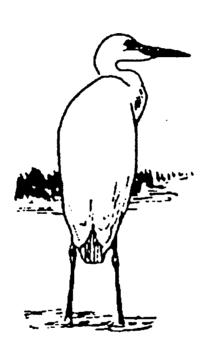
# SQUAW CREEK NATIONAL WILDLIFE REFUGE CONTAMINANT SURVEY RESULTS

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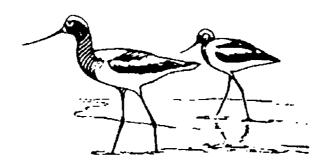
#### EXECUTIVE SUMMARY

As part of a baseline contaminant survey of all National Wildlife Refuges (NWR) in Missouri, fish were collected at the Squaw Creek NWR from Davis and Squaw creeks in August, 1987. Standard metals and organochlorine scans were completed on these samples.

The results were compared to the nationwide geometric mean for each metal and organochlorine, as established by the U.S. Fish and Wildlife Service's (Service) database, the National Contaminant Biomonitoring Program. Individual samples were found to have levels of arsenic, cadmium, copper, lead, mercury, selenium, zinc, or dieldrin greater than the national average. ( PCBP)

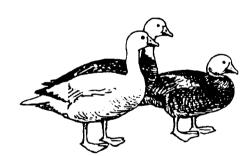
Arsenic, cadmium, and zinc were highly elevated. A follow-up study is recommended with emphasis on these three metals. A common link among these three contaminants is lead. Lead is associated with arsenic, cadmium, and zinc in the form of dry or wet cell batteries, and/or in refining or recycling of lead. A battery recycling plant located near Squaw Creek NWR has been a source of local controversy in recent years. Therefore, lead should be emphasized in a follow-up study as well.

Should elevated levels of these metals be detected in the follow-up study, an intensive, detailed investigation is warranted to determine whether the contaminants are moving through the food chain and affecting Service trust resources. Since the primary purpose of the refuge relates to avian species, with emphasis on endangered species, waterfowl and shorebirds, measures should be taken to protect these resources consistent with further findings.



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# Squaw Creek National Wildlife Refuge

## Contaminant Survey Results

#### Introduction

This report presents the results of sampling efforts conducted over the past several years on Squaw Creek National Wildlife Refuge (NWR), Missouri. Similar reconnaissance-level studies have been conducted on all NWR's and Neosho National Fish Hatchery in Missouri. Results of investigations conducted on each Fish and Wildlife Service (Service) facility, as well as recommendations for future actions, are outlined in companion reports.

## Study Area Description

The study area is near Mound City, Holt County, in northwestern Missouri (Fig. 1). This NWR is administered by the Service and consists of approximately 7,178 acres. The refuge is influenced by a total watershed area in excess of 63,200 acres. Several creeks contribute to this total watershed; these creeks watershed areas are: Squaw Creek 46,000 acres, Davis Creek 15,000 acres, and Little Tarkio Creek and three smaller creeks combined approximately 2,200 acres. Man applied chemicals are a potential threat to fish and wildlife in the study area. The study area located at the junction of the several creeks increases the likelihood of contaminant concentrations.

Most of the NWR is very low and flood prone. Levees offer flood protection except when water levels are extremely high. According to a 1939 survey three soil types are found on the study area. They are 1)Wabash clay, ponded phase in the south bottomlands, 2)McPaul silt loam 0-4% slope in the north bottomlands, and 3)Hamburg very fine sandy loam 30-50% slope in the bluffs. Presently, about 7% of the area is farmed. A three crop rotation of winter wheat, corn, and soybeans is used.

The State of Missouri owns the Bob Brown Wildlife Area, Big Lake State Park, Bigalow 'Pond' and adjacent lands all located within a 6 mile radius of Squaw Creek NWR. These lands are being intensively managed for waterfowl usage.

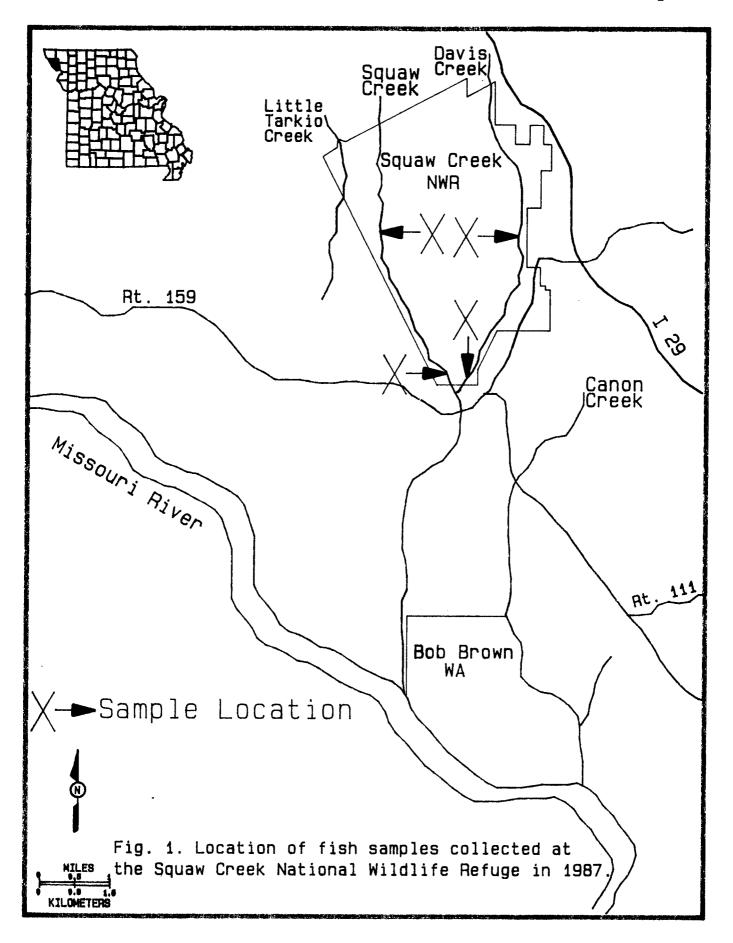
## Relationship to Other Studies

Several site visits were conducted over the past 7 years by the Columbia, Missouri Field Office (CMFO) contaminant biologist. Appendix A contains a map of the Service collection sites from 1985 through 1990 and a table relating the studies to the collection points.

In 1985, at the request of Representative Tom Coleman, CMFO conducted a limited sampling program at Squaw Creek NWR and around the Schuylkill Metals Corporation facility. The results of this sampling (Appendix B) indicated that lead contamination problems exist at and around the Schuylkill facility. Appendix C contains a Missouri Department of Conservation memorandum summarizing the studies relating to the Schulykill facility.

In May 1987, a sampling proposal was submitted (Appendix D) that included the justification for this study. The sampling proposal was for the purpose of determining baseline data for three NWR's and one National Fish Hatchery (NFH) in Missouri.

In July 1988, the Missouri Department of Health analyzed water samples from domestic water well located on the Squaw Creek NWR. They analyzed for five



pesticides: atrazine, alachlor, chlorpyrifos, metolachlor, and trifluralin. None were detected.

In January 1990, deer liver and kidney samples were collected by the CMFO contaminant specialist at Squaw Creek NWR. These collections were made to corroborate the findings from studies conducted by the Missouri Western State College (MWSC) personnel. For several years Dr. R.J. Robbins and his students have been collecting kidneys and reproductive tract samples from deer harvested in primitive weapons hunts at the NWR. Data from both the MWSC and Service studies are unpublished data to date.

In April 1990, fish samples were collected at Squaw Creek NWR by CMFO and were analyzed for the presence of dioxin. Dioxin was not detected in any of the samples. This also is unpublished data.

The United States Environmental Protection Agency currently has a contractor performing an extensive biological study at the Schulykill facility and surrounding area, including the Squaw Creek NWR.

#### Methods

## Collection Methods

The actual sample collection locations are indicated in Figure 1 and in Appendix A. Sample locations were chosen where the two main water sources (Davis and Squaw Creeks) enter and leave the NWR. These sites were chosen to determine the potential sources of contaminants. Fish samples, collected in August 1987, were obtained from all four locations.

Collections of fish were made at all sites (Fig. 1). Seining and gill netting methods were used. These methods were continued until adequate samples were obtained. When selecting fish from the nets, preference was given to those species that tend to be high in fat, such as carp, buffalo, and catfish. Each fish was weighed to the nearest 0.1 gram and total length was measured to the nearest millimeter.

Each fish was then individually wrapped in aluminum foil, labeled and stored on ice in a cooler until returning to CMFO. The specimens were then frozen in a chest style freezer unit. Eventually, they were shipped in coolers with dry ice to the appropriate contract laboratory for analysis. The shipment was accompanied by a catalog containing instructions, types of analyses, and specific sample information (Appendix E).

One snapping turtle was collected by hand. Upon returning to CMFO, the liver was dissected out of the carcass and placed in a chemically cleaned glass jar. The sample was then handled in the same manner as the fish.

Tables relating the sample number to the site location number are located in Appendix F for metals and Appendix G for organochlorines.

## Laboratory Methods

An atomic absorption (AA) spectrophotometer technique was used for measuring levels of arsenic, mercury, and selenium. All other metals (cadmium, copper, iron, lead, molybdenum, nickel, thallium, vanadium, and zinc) were detected with an inductively coupled plasma atomic emission spectrophotometer (ICP).

Chemical analysis for organochlorines (alpha-BHC, alpha-Chlordane, beta-BHC, cis-Nonachlor, o,p'-DDD, p,p'-DDD44, o,p'-DDE, p,p'-DDE, o,p'DDT, p,p'DDT, del-BHC, dieldrin, endrin, gamma-Chlordane, HCB, heptachlor-epoxide, lindane/gamma-BHC, mirex, oxy-chlordane, PCB (total), toxaphene, trans-Nonachlor) was accomplished by gas-liquid chromatography after extraction, gel permeation chromatography cleanup, and silica gel chromatography separation.

The Environmental Trace Substances Research Center in Columbia, Missouri, performed the analyses for metals and the Mississippi State Chemical Laboratory at Mississippi State University performed the analyses for organics. These laboratories are under contract to the Service and were subjected to a rigorous evaluation process prior to the award of their contracts. The Patuxent Analytical Control Facility of the Service closely monitors the performance of these laboratories during analysis and has confidence in the accuracy of the data. Acceptable performance on spikes, blanks, and duplicates was documented in laboratory quality control reports.

#### Results and Discussion

It is not a simple task to accurately measure concentrations of contaminants in tissues of fish and wildlife. However, once the concentrations have been correctly measured, it is sometimes even more difficult to determine what these concentrations mean to the well-being of the organism or to predatory species of fish and wildlife which may consume the organism. Detailed information on this subject is sparse [1].

There are no uniformly accepted standards for tolerable tissue concentrations of contaminants which will protect fish and wildlife and the predators which consume them. Instead, there is a hodgepodge of action and alert levels proposed by various agencies and experts for specific rather than uniform applications [1].

Some of these action or alert levels are based on fillet (edible to humans) samples, while others are based on whole-body samples. Some relate to fish only. For the contaminants which have been relatively extensively studied, like PCB's, we have many action or alert levels for comparison with our residue data. Very few or no alert levels for residues in fish and wildlife matrices have been proposed for many other contaminants, especially those for which effects have not been well documented. Therefore, less is known about the potential meaning of these residue values [1].

After an extensive literature review and consulting with numerous Service experts, including chemists, toxicologists, and biologists, basically one data set was selected for contaminant comparison of background or threshold levels. The data set is the National Contaminant Biomonitoring Program (NCBP), which is maintained by the Service and documents temporal and geographic trends in concentrations of persistent environmental contaminants that may threaten fish and wildlife resources (Table 1) [2,3].

## Sampling Results Summary -

Metals were detected in all of the fish samples and in the turtle liver sample. Metals that were found in these samples above the laboratory detection limits were arsenic, cadmium, copper, iron, lead, mercury, molybdenum, nickel, selenium, thallium, vanadium, and zinc.

Organochlorines were detected in all but one of the fish samples. Organochlorines that were found in fish above the laboratory detection limits

were Alpha-Chlordane, cis-Nonachlor, DDD, DDE, Dieldrin, Gamma-Chlordane, Heptachlor-epoxide, and trans-Nonachlor.

Contaminants that were reported above laboratory detection limits are shown in Appendix F for metals and Appendix G for organochlorines. Each contaminant detected is listed at the sites where they were found. The maps in Appendix F and Appendix G also list the levels of contaminants discovered at each location with a separate map for each contaminant.

Table 1. Background levels of various contaminants in whole body fish from the 1984 National Contaminant Biomonitoring Program (NCBP) reported as the wet weight geometric mean (ppm) for the nationwide data set.

CONTAMINANT	GEOMETRIC MEAN CONCENTRATION	CONTAMINANT	GEOMETRIC MEAN CONCENTRATION
ARSENIC	0.14	DDD, DDE, DDT - T	OTAL 0.26
CADMIUM	0.03	DIELDRIN	0.04
COPPER	0.65	ENDRIN	<0.01
LEAD	0.11	нсв	<0.01
MERCURY	0.10	HEPTACHLOR EPOX	IDE 0.01
SELENIUM	0.42	MIREX	<0.01
ZINC	21.7	TOXAPHENE	0.14
внс	<0.01	PCBs - TOTAL	0.39
CHLORDANE - TOTAL	0.11		

The complete report of the sample analyses for both metals and organochlorines is on file at the Squaw Creek NWR; listed in Table 2 and Table 3 are the analytical results for those contaminants that were above detection limits in at least one sample.

A brief discussion of the results of metals and organochlorine analyses of the samples from Squaw Creek NWR is provided below. Results from other NWR's and the Neosho National Fish Hatchery (NFH) also are provided for purposes of comparison. All results reported are in dry weight (ppm) unless otherwise indicated.

#### Metals Results -

Arsenic (As, CAS Number 7440-38-2)

Arsenic was detected from 11 of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from 0 to 3.90 ppm. Fish were sampled at four NWR's and the NFH located in Missouri, with the highest level of arsenic, 3.90 ppm, detected from Squaw Creek NWR.

The 3.90 ppm dry weight sample converted to wet weight is 1.09 ppm. This is an elevated level. The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.14 ppm wet weight [2]. Elevated levels were detected in three of the Squaw Creek NWR fish samples from three of the sample sites.

215.00

103.00

1.50

2.20

Table 2. Metals concentrations in whole fish that were above detection limits, ppm dry weight.

SAMPLE NUMBER	ARSENIC	CADMIUM	COPPER	IRON	LEAD	MERCURY
55850035	0.20	0.17	2.75	411.00	ND	0.08
55850036	ND*	0.19	2.75	345.00	ND	0.16
55850037	3.90	0.10	4.10	1360.00	0.70	0.05
55850038	ND	0.26	4.43	429.00	ND	0.20
55850039	1.60	0.44	4.81	1090.00	1.00	0.35
55850040	0.30	0.14	3.31	266.00	ND	0.24
55850041	ND	0.64	4.51	554.00	ND	0.87
55850042	0.30	0.62	5.03	414.00	ND	0.16
55850043	ND	0.16	11.00	1250.00	ND	1.30
55850044	0.50	0.20	4.77	639.00	0.50	0.27
55850045	0.66	0.29	4.29	973.00	ND	0.54
55850046	0.50	0.45	2.30	573.00	ND	0.16
55850047	0.50	0.25	2.78	680.00	ND	0.16
55850048	ND	0.13	3.59	228.00	ND	0.38
55850049	0.40	0.15	3.10	127.00	ND	0.11
55850050	0.30	0.13	3.82	604.00	ND	0.22
55850051	ND	0.20	4.31	343.00	ND	0.81
SAMPLE NUMBER	MOLYBDENUM	NICKEL	SELENIUM	THALLIUM	VANADIU	1 ZINC
55850035	ND	2.90	1.00	ND	1.60	75.70
55850036	ND	1.70	1.90	ND	0.68	102.00
55850037	ND	4.90	1.00	ND	4.46	47.60
55850038	ND	3.30	2.00	ND	1.20	194.00
55850039	ND	3.70	2.00	ND	2.30	256.00
55850040	ND	2.80	1.00	ND	0.35	191.00
55850041	ND	3.20	2.30	ND	0.95	219.00
55850042	0.77	12.00	2.00	ND	0.26	164.00
55850043	0.50	0.50	2.90	ND	0.37	91.40
55850044	ND	3.40	1.00	ND	2.60	97.70
55850045	ND	3.60	0.80	ND	2.90	99.80
55850046	ND	1.60	2.60	ND	1.20	87.10
55850047	ND	4.00	2.50	ND	2.00	93.70
55850048	ND	1.40	1.00	ND	0.47	240.00
55850049	0.10	1.40	2.00	ND	0.51	188.00
					1 50	215 00

2.10

0.90

ND

ND

ND

55850050

55850051

2.30

2.80

<sup>\*</sup> ND - Nondetectable level

Table 3. Organochlorine concentrations in whole fish that were above detection limits, ppm dry weight.

SAMPLE NUMBER	CHLORDANE TOTAL**	DDX* TOTAL	DIELDRIN	HEPTACHLOR EPOXIDE
55850035	0.06	0.03	0.10	0.02
55850036	0.03	0.01	0.04	0.01
55850037	0.06	0.04	0.18	0.03
55850038	0.03	0.03	0.06	0.01
55850039	0.03	0.04	0.04	0.01
55850040	0.06	0.04	0.14	0.02
55850041	0.04	0.03	0.06	0.01
55850042	0.02	0.02	0.07	0.01
55850043	ND***	ND	ND	ND
55850044	0.03	0.03	0.05	ND
55850045	0.03	0.02	0.05	0.01
55850046	0.03	0.02	0.06	0.01
55850047	0.03	0.01	0.04	ND
55850048	0.08	0.03	0.13	0.02
55850049	0.01	0.01	0.01	ND
55850050	0.04	0.02	0.11	ND
55850051	ND	ND	ND	ND

- \* Total DDD, DDE, DDT
- \*\* Total Chlordane Isomers
- \*\*\* ND Nondetectable level

## Cadmium (Cd, CAS Number 7440-43-9)

Cadmium was detected in all of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from 0.10 to 0.64 ppm. Fish were sampled at four NWR's and the NFH located in Missouri with the highest level of cadmium, 2.96 ppm, reported from Clarence Cannon NWR.

The 0.64 ppm dry weight sample converted to wet weight is 0.17 ppm. This is an elevated level. The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.03 ppm wet weight [2]. Elevated levels were detected in 15 of the fish samples, and from all of the sample sites at Squaw Creek NWR.

## Copper (Cu, CAS Number 7440-50-8)

Copper was detected in all of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from 2.30 to 5.03 ppm. Of the fish samples from the four NWR's and Neosho NFH in Missouri, the highest level of copper was 60.10 ppm at Clarence Cannon NWR.

The 5.03 ppm dry weight sample converted to wet weight is 1.37 ppm. This is an elevated level. The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.65 ppm wet weight [2].

Elevated levels were detected in 14 of the fish samples, and from all of the sample sites at Squaw Creek NWR.

#### Iron (Fe)

Iron was detected in all of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from 127 to 1,360 ppm. Fish were sampled at four NWR's and the NFH located in Missouri. The highest level of iron was the 1,360 ppm sample from Squaw Creek NWR.

There is not sufficient information in the literature to make comparisons of whole body fish concentrations of iron.

## <u>Lead</u> (Pb, CAS Number 7439-92-1)

Lead was detected in three of the 16 fish samples from three of the four sample sites at Squaw Creek NWR. The concentrations ranged from 0.50 ppm to 1.00 ppm. Fish sample results from the four NWR's and the NFH located in Missouri yielded a high level 4.4 ppm lead (dry weight) from Mingo NWR.

The 1.00 ppm dry weight sample converted to wet weight is 0.235 ppm. This is an elevated level based on comparison with the geometric mean for whole fish samples from 109 NCBP stations of 0.11 ppm wet weight [2]. Elevated levels were detected in three of the fish samples from three of the sample sites at Squaw Creek NWR.

#### Mercury (Hq, CAS Number -Hydragyrum- 7439-97-6)

Mercury was detected in all of the 16 fish samples from Squaw Creek NWR. The concentrations ranged from 0.05 to 0.87 ppm. The highest level of mercury from the four NWR's and the NFH located in Missouri was 5.51 ppm from Mingo NWR.

The 0.87 ppm dry weight sample, converted to wet weight is 0.20 ppm, is an elevated level. The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.10 ppm wet weight [2]. Elevated levels were detected in four of the fish samples from three sample sites at Squaw Creek NWR.

## Molybdenum (Mo, CAS Number 7439-98-7)

Molybdenum was detected in two of the 16 fish samples from two of the four sample sites at Squaw Creek NWR. The concentrations ranged from 0.10 ppm to 0.77 ppm. These values compare to the highest level of molybdenum found in samples from the four NWR's and Neosho NFH located in Missouri of 0.81 ppm dry weight at Neosho NFH.

There is not sufficient information in the literature to make comparisons of whole body fish concentrations for molybdenum.

Nickel (Ni, CAS Number 7440-02-2)

Nickel was detected in all of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from 1.40 ppm to 12.00 ppm. Fish sampled at four NWR's and the NFH located in Missouri yielded a high level of nickel of 123.00 ppm from Neosho NFH.

There is not sufficient information in the literature to make comparisons of whole body fish concentrations for nickel.

Selenium (Se, CAS Number 7782-49-2)

Selenium was detected in all of the 16 fish samples from all four sample sites at Squaw Creek NWR. The concentrations ranged from 0.80 ppm to 2.60 ppm. The highest level of selenium in fish from four NWR's and the NFH in Missouri was 2.90 ppm at Neosho NFH.

The 2.60 ppm dry weight sample converted to wet weight is 0.59 ppm. Compared to the geometric mean for whole fish samples from 109 stations nationwide in the NCBP (0.42 ppm wet weight [2]), this is an elevated level. Elevated levels were detected in 10 of the fish samples from all of the sample sites at Squaw Creek NWR.

#### Thallium (Tl)

Thallium was not detected in fish samples from any of the Squaw Creek sample sites.

Vanadium (V, CAS Number 1314-62-1)

Vanadium was detected in all of the 16 fish samples from Squaw Creek NWR. The concentrations ranged from 0.35 to 4.46 ppm. The 4.46 ppm sample was the highest of all samples collected from the four NWR's and the NFH located in Missouri.

There is not sufficient information in the literature to make comparisons of whole body fish concentrations of vanadium.

Zinc (Zn, CAS Number 7440-66-6)

Zinc also was detected in all of the 16 fish samples from Squaw Creek NWR. The concentrations ranged from 47.60 to 256.00 ppm. The highest level of zinc detected from the NWR's and NFH in Missouri, however, was 375.00 ppm from samples collected at Clarence Cannon NWR.

The 256.00 ppm dry weight sample converted to wet weight is 60.16 ppm. This is an elevated level based on a comparison with the geometric mean for whole fish samples from 109 stations nationwide (NCBP) of 21.70 ppm wet weight [2]. Elevated levels were detected in 12 of the fish samples and from all of the sample sites at Squaw Creek NWR.

## Metals Discussion -

Metals occur in natural waters in trace amounts. Since metals are used extensively in many industrial processes, they are usually present in a

variety of effluents entering ground and surface waters. Reisinger [4] notes that while some metals are essential to aquatic biota in trace amounts, the concentrations found in metal-enriched ecosystems are potentially harmful. Under some conditions, metals in suspension are toxic to fish, but in general it is the metallic ion in solution which exhibits toxicity to living organisms. Organisms exposed to sublethal metal concentrations have shown increased tolerance in subsequent exposures [5,6].

Dissolved organic matter (DOM) plays a significant role in the distribution, transport and fate of heavy metals in aquatic systems. Dissolved organics are capable of complexing metals and increasing solubility; altering distribution between oxidized and reduced forms; and influencing the extent to which metals are adsorbed on suspended matter. When metals are present in small amounts, DOM can make the metal either more or less available to an organism. However, the toxic effects of metals present in high concentrations can be alleviated by DOM [6,7].

When an aquatic food chain is contaminated, bioconcentration, bioaccumulation, and biomagnification can occur. Metals entering an organism will be transported to organs ("target organs") for which a particular metal has an affinity. In aquatic organisms, an equilibrium mechanism appears to regulate metal uptake, and once equilibrium has been reached, body or organ concentrations will shift only with a shift in source concentration [4,6].

The incorporation of metals into fish can occur along two pathways: 1) absorption across gill surfaces, and 2) through the gut wall. Investigations suggest that the gastrointestinal route becomes less important as an aquatic ecosystem becomes progressively contaminated with metals [8]. There is experimental evidence which demonstrates homeostatic regulation of calcium, magnesium and zinc in fish [8]. This suggests that fish are of decreased value for monitoring metals when body concentrations are independent of ambient concentrations and should be used to monitor only for metals known to accumulate with exposure [6].

Many external factors influence the absorption and toxicity of metals to fish. These factors include the nature and concentration of the metal, its valence, the form of the metal in water, presence of other metals, pH, volume of water, time and duration of exposure, water temperature, dissolved oxygen levels, and the feeding habits and physical condition of the fish. In addition, differences occur among fish species with respect to their ability to concentrate metals [6].

## Organochlorine Results -

## BHC (beta-BHC, beta Benzene Hexachloride) Lindane

BHC's, including Lindane, were not detected in fish at any of the Squaw Creek NWR sites.

# Chlordane (CAS Number -Aspon, Belt- 57-74-9)

Total chlordane was detected in 15 of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from non-detectable to 0.08 ppm. Fish were sampled at four NWR's and the NFH located in Missouri, with the highest level of chlordane (0.24 ppm wet weight) indicated from Neosho NFH.

The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.11 ppm wet weight [3]. Therefore, the levels from Squaw Creek samples are not considered to be elevated.

DDX DDD (p,p' DDD CAS Number 72-54-8) DDE (p,p' DDE CAS Number 72-55-9) DDT (p,p' DDT, CAS Number 50-29-3)

DDX was detected in 15 of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from non-detectable to 0.04 ppm wet weight. Fish sampled at four NWR's and the NFH in Missouri yielded a high level of 0.15 ppm wet weight DDX from Neosho NFH.

The geometric mean for whole fish samples from 109 stations nationwide in the NCBP was 0.26 ppm wet weight for total DDD, DDE and DDT [3]. None of the Missouri samples appears to be elevated according to this criterion.

## Dieldrin (CAS Number -Alvit- 60-57-1)

Dieldrin was detected in 15 of the 16 fish samples from all four of the sample sites at Squaw Creek NWR. The concentrations ranged from non-detectable to 0.18 ppm wet weight. The highest level of dieldrin from all five Missouri NWR and NFH locations was 1.50 ppm wet weight at Swan Lake NWR.

The 0.18 ppm wet weight sample from Squaw Creek NWR is an elevated level compared to the NCBP geometric mean for whole fish samples of 0.04 ppm [3]. Elevated levels were detected in 11 of the fish samples taken from all of the sample sites at Squaw Creek NWR.

## Endrin (Compound 269, CAS 72-20-8)

Endrin was not detected in fish from any of the Squaw Creek NWR sites.

## HCB Hexachlorbenzene (HCB, CAS 118-74-1)

HCB was not detected in fish from any of the Squaw Creek NWR sites.

#### Heptachlor Epoxide

Heptachlor Epoxide was detected in 11 of the 16 fish samples from all four of the sample sites at Squaw Creek NWR, with concentrations ranging from non-detectable to 0.03 ppm wet weight. Fish samples from four NWR's and the NFH located in Missouri yielded a high level of 0.06 ppm heptachlor epoxide from Swan Lake NWR.

These levels of concentration are below elevated levels when compared with NCBP data.

## Mirex (Dechloran, CAS 2385-85-5)

Mirex was not detected from fish at any of the Squaw Creek NWR sites.

PCBs (Polychlorinated Biphenyls, CAS Number 53469-21-9)

PCBs were not detected from fish at any of the Squaw Creek NWR sites.

Toxaphene (CAS Number -Attac, Vertac, Camphechlor- 8001-35-2)

Toxaphene was not detected from fish at any of the Squaw Creek NWR sites.

## Organochlorine Discussion -

For many years pesticides have been one of the most highly publicized classes of environmental pollutants. Chlorinated hydrocarbon insecticides such as DDT, dieldrin, endrin, heptachlor, and others, including their metabolites, share three characteristics which cause their use to be of ecological significance.

Biologically, they are very active and their toxicity, rather than being restricted to insects, extends to a large variety of organisms, including vertebrates. They are chemically very stable and therefore often persist within the environment for years, either in their original state or in a slightly modified state. The non-polar character of these compounds gives them low water solubility and a high lipid solubility, increasing the risk to aquatic organisms [6].

Chlorinated hydrocarbon pesticides (organochlorines) came into wide use in the 1940's. This has resulted in measurable concentrations of organochlorines in practically all surface waters of the world [9]. Pesticides have been identified in soils, sediments, aquifers, lakes, ponds, rivers and streams, as well as the oceans. Antarctic snow and air are contaminated with pesticides [7]. Pesticides have also been found in a wide range of organisms, and there is evidence that they contribute to fish diseases [6,7].

Pesticides may gain access to ground and surface waters through direct application, through percolation and runoff from treated areas, and through drift during application. Additional sources of pesticides in the aquatic environment are pesticide manufacturing and associated waste discharges, improper disposal of containers, and accidental spills [6].

Similar in structure to some chlorinated pesticides, polychlorinated biphenyls (PCBs) are a group of synthetic compounds with worldwide distribution. They are released into the environment through spills, effluent discharges, incineration, or through disposal in dumps and landfills. Their thermal and chemical stability causes them to be long-term environmental problems. They degrade slowly over a period of many years. However, they are absorbed readily by living organisms, accumulating in lipid tissues and continuing to increase over time, even though exposure levels decrease. This bioaccumulation can cause direct acute impacts. Chronic effects on growth, reproduction, behavior, and general health have been reported in fish, birds, and mammals. Fish are particularly susceptible since they concentrate PCBs to levels known to cause toxicological impacts to piscivorous fish and wildlife species [6].

#### Conclusions

The results from the Squaw Creek NWR study were compared to the NCBP geometric mean for each contaminant [2,3]. These are indicative of background levels in fish. Based upon the limited sampling in this survey, elevated levels were shown for arsenic, cadmium, copper, lead, mercury, selenium, zinc, and dieldrin.

The highest elevated level recorded during this survey for each of these contaminants in fish is arsenic 3.9 ppm, cadmium 0.64 ppm, copper 5.03 ppm, lead 1.0 ppm, mercury 0.871 ppm, selenium 2.6 ppm, zinc 256 ppm, and dieldrin 0.18 ppm (all of these results are in dry weight except dieldrin). Refer to the results section of this document for contaminant level comparisons. Appendix H contains a comparison of these levels to other Service facilities in Missouri.

Differences in the levels of contaminants detected at the upper and lower sites at both the Squaw Creek and Davis Creek sample sites were inclusive with the small data set available. A comparison of the elevated levels from the Squaw Creek NWR survey was made with geometric mean values reported from the 109 station NCBP [2,3]. To help understand the degree of elevation of the Squaw Creek sample results, Table 4 below indicates the percentage of these values above the NCBP data.

Table 4. Comparison of highest Squaw Creek NWR 1987 levels to National Contaminant Biomonitoring Program (NCBP) geometric means.

Contaminant	Highest Level (ppm wet weight)	NCBP Geo. Mean (ppm wet weight)	Percent Above NCBP Geo. Mean
Arsenic	1.09	0.14	780 %
Cadmium	0.17	0.03	563 <b>%</b>
Copper	1.37	0.65	211 %
Lead	0.23	0.11	214 %
Mercury	0.20	0.10	201 %
Selenium	0.59	0.42	140 %
Zinc	60.16	21.70	277 %
Dieldrin	0.18	0.04	450 %

Detailed discussion and citations may be found in Appendix I of this report for the following seven metals and dieldrin, which are considered to be elevated at Squaw Creek NWR.

<u>Arsenic</u> is highly elevated. In the NCBP study, 85% of the arsenic results nationwide were below 0.27 ppm wet weight. Elevated concentrations of arsenic can result in decreased growth in mallard ducks. Arsenic enters streams and eventually the sediments and biota from air pollution, soil erosion, pesticides, and industrial sources. One source of elevated levels at Squaw Creek NWR could be from historical use of arsenical agricultural chemicals in the intensively farmed upstream watershed. Arsenic also is produced as a byproduct of copper, lead, and zinc smelters.

<u>Cadmium</u> also is highly elevated. In the NCBP study, 85% of the cadmium results nationwide were below 0.05 ppm wet weight. Mammals and birds consuming cadmium-contaminated food have experienced lowered sperm counts,

kidney damage, increased mortality of young, elevated blood sugars, and anemia. Some sources of cadmium are air pollution from smelters and incinerators, metal plating operations, sewage sludges, and leachates from municipal landfills.

Copper is elevated. In the NCBP study, 85% of the copper results nationwide were below 1.0 ppm wet weight. In water, copper acts synergistically with other common urban contaminants, such as ammonia, cadmium, mercury, and zinc, to produce an increased toxic effect on fish. Copper is one of the most common contaminants associated with urban runoff; other sources of copper could be fungicides, fertilizers, sewage treatment plant discharges, and landfills.

Lead is elevated; however, the high value (0.23 ppm wet weight) in this study is lower than the high value (0.34 ppm wet weight) in a 1985 study conducted by this office. In the NCBP study, 85% of the lead results nationwide were below 0.22 ppm wet weight. Lead is very toxic to aquatic organisms, with fish being the most sensitive. All measured effects of lead on living organisms are adverse, including those negatively affecting survival, growth, learning, reproduction, development, behavior, and metabolism. Sources of lead in the study area are mainly from airborne emissions. There also may be some residual lead contamination from previous extensive usage of leaded gasoline. A nearby battery recycling plant may contribute to lead levels as well.

Mercury is elevated. In the NCBP study, 85% of the mercury results nationwide were below 0.17 ppm wet weight. Mercury biconcentrates and biomagnifies; it has only harmful effects, with no useful physiological functions when present in fish and wildlife. Mercury is a carcinogen, mutagen, and a teratogen. Sources of mercury include batteries, sewage treatment discharges, paints, pesticide compounds, smelters, and landfill leachates. Mercury and selenium are antagonistic, reducing the other's toxicity.

Selenium is slightly elevated. In the NCBP study, 85% of the selenium results nationwide were below 0.73 ppm wet weight. This is higher than the highest selenium level recorded in the Squaw Creek NWR study (0.59 ppm wet weight). Selenium is an essential trace element in animal diets, but the range between nutritional requirements and toxic levels is relatively narrow. Sources of selenium include soil erosion, sewage sludge, air pollution from metal smelting and coal fired power plants.

Zinc is elevated. In the NCBP study 85% of the zinc results nationwide were below 34.2 ppm wet weight. Zinc is an essential trace element in plant and animal life; however, there have been cases of high zinc levels being toxic to fish and wildlife. Sources of zinc include soil erosion, both dry and wet cell batteries, pesticides, rubber tires, and sewage sludge.

<u>Dieldrin</u> is elevated. Dieldrin is toxic to fish, bioaccumulates in fish, and is very persistent. Even though no dieldrin has been used for agricultural purposes since 1974, the NCBP study has shown no significant decrease in nationwide dieldrin levels.

## Recommendations

A follow-up study should be conducted with emphasis on arsenic, cadmium and zinc. One common link with these three contaminants is the presence of lead. Therefore, lead also should be emphasized. This study should include fish, sediment, and soil samples. The sediment and soil samples should be from Squaw and Davis Creeks, as well as from interior locations on Squaw Creek NWR.

Should elevated levels continue to be detected, a more detailed study is warranted to determine whether the contaminants are moving up the food chain and affecting avian wildlife. Since the primary purpose of the Squaw Creek NWR relates to avian species, with emphasis on federally-listed species, waterfowl and shorebirds, measures should be taken to determine any significant impact to these resources and methods to effect their protection.

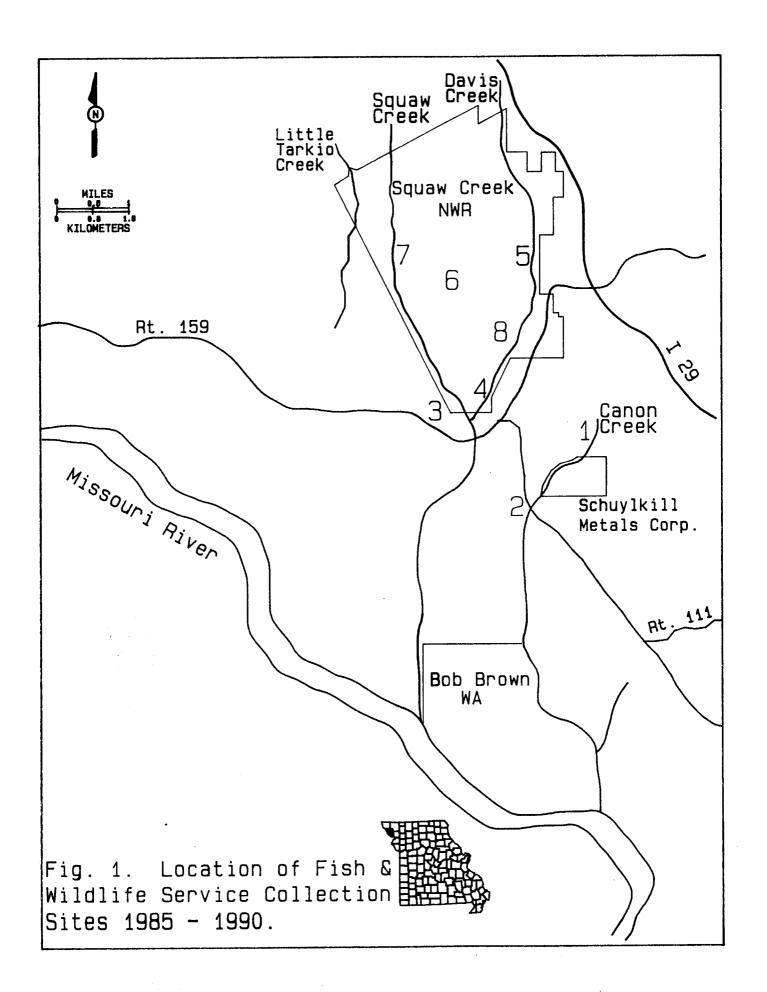
A 1987 fishery management assessment of Squaw Creek NWR recommended no further attempts to enhance the sport fishery. Therefore, future contaminant studies that include fish sampling will relate to fish only as part of the food chain affecting higher level predators, such as the bald eagle, and not for human consumption. Emphasis will probably be on small mammals and waterfowl, which form a larger part of the diet of bald eagles and other raptors than do fish.

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TJN:tn:1110/HOSQUAWA

Appendix A Fish & Wildlife Service Sample Collection Sites 1985 - 1990



# FWS Collection Sites 1985 - 1990

Year	Sites Sampled
1985	1, 2, 3, 4, 5, 6
1987	3, 4, 5, 7
1990	8
1990	4